

## Chem 352 - Fall 2018 - Exam I

Some potentially useful information:

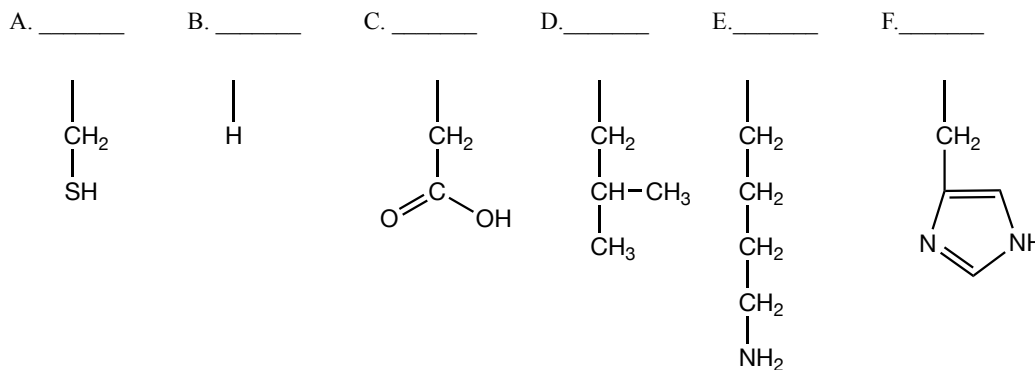
$pK_a$  values for ionizable groups in peptides and proteins: ( $\alpha$ -carboxyl, 3.46;  $\alpha$ -amino, 7.87; and the side chains of *Asp*, 4.03; *Glu*, 3.62; *His*, 6.71; *Cys*, 8.4; *Tyr*, 10.33; *Lys*, 10.21; *Arg*, 12.01)

$$R = 8.314 \text{ J/(mol}\cdot\text{K)} = 0.08206 \text{ (L}\cdot\text{atm)/(mol}\cdot\text{K)}$$

1. Match the following pioneers in the field of biochemistry with the contributions they each made:

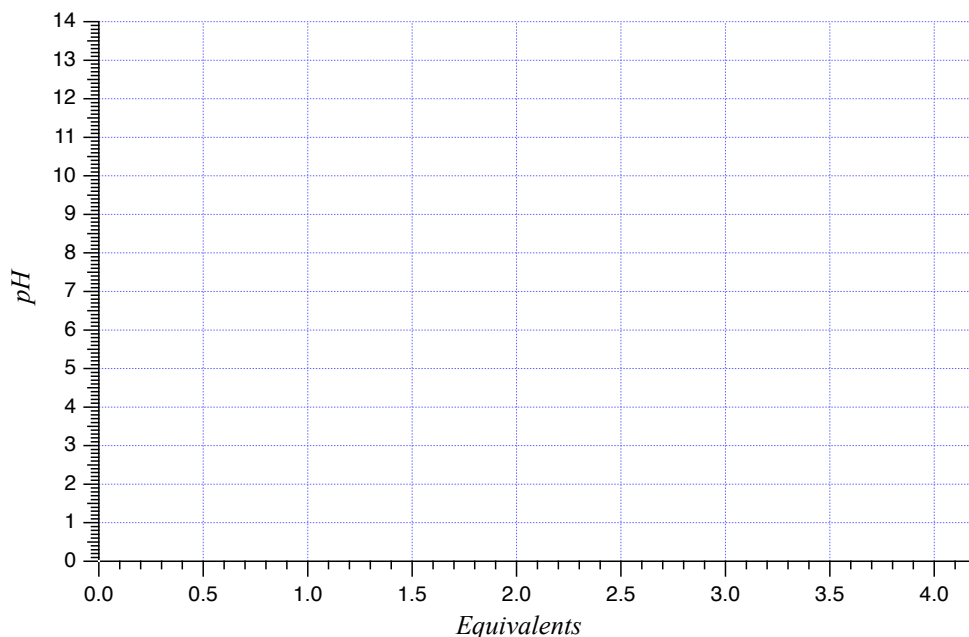
- |                          |   |
|--------------------------|---|
| a. ____ James Watson     | A. Received a Nobel Prize for characterizing the chemical structures of simple sugars, and purines, which are components of nucleic acids.                          |
| b. ____ Linus Pauling    | B. Was one of the first people to determine the 3-D structure of a protein, for which he shared a Nobel Prize.  |
| c. ____ Frederick Sanger | C. Shared a Nobel Prize for proposing a structure for DNA.  |
| d. ____ Eduard Buchner   | D. Received two Nobel Prizes in Chemistry, one for developing a method to sequence polypeptides and another for developing a method to sequence polynucleotides.    |
| e. ____ Emil Fischer     | E. Was first to propose the $\alpha$ -helical and $\beta$ -sheet secondary structures in proteins. He also received two Nobel Prizes for unrelated accomplishments. |
| f. ____ Max Perutz       | F. Demonstrated that living yeast cells were not required to carry out fermentation reactions. It could be accomplished with cell-free extracts from yeast.         |

2. Using the three-letter abbreviations, identify each of the following amino acid side chains.



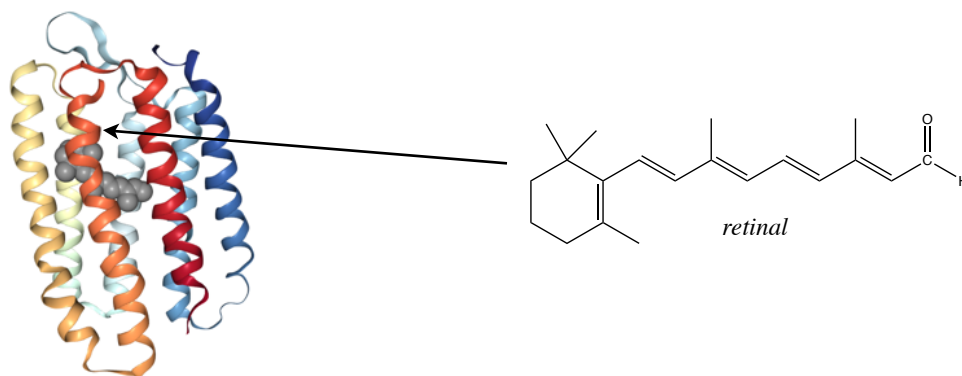
- |   |   |   |   |   |   |   |
|---|---|---|---|---|---|---|
| a. Which of these can hydrogen bond to water? ( <i>Circle all that apply.</i> ) | A | B | C | D | E | F |
| b. Which of these is charged at $pH$ 2? ( <i>Circle all that apply.</i> )       | A | B | C | D | E | F |
| c. Which of these is charged at $pH$ 9? ( <i>Circle all that apply.</i> )       | A | B | C | D | E | F |
| d. Which of these is considered hydrophobic? ( <i>Circle all that apply.</i> )  | A | B | C | D | E | F |
| e. Which of these can form disulfide bonds? ( <i>Circle all that apply.</i> )   | A | B | C | D | E | F |

3. GHK-Cu is a tripeptide with the sequence Gly-His-Lys that strongly binds copper(II) ions. GHK-Cu is proposed to have a range of different biological effects, including an ability to promote wound healing, attract immune cells, stimulate collagen and glycosaminoglycan synthesis in skin fibroblasts, and promote blood vessel growth.
- Based on this description, draw the chemical structure for the isoelectric form of GHK-Cu in water. (The  $pK_a$ 's for the ionizable groups on amino acids can be found on p.1.)
  - Circle all of the chiral carbons in your structure.
  - Label one example each of a  $\phi$ , a  $\psi$ , and an  $\omega$  bond in your structure.
  - What is the isoelectric  $pH$  ( $pI$ ) for GHK-Cu? \_\_\_\_\_
  - Using the  $pK_a$ 's provided, calculate the  $pH$  of a 200 mM solution of the fully protonated form of GHK-Cu. (Show your calculation below.)  $pH =$  \_\_\_\_\_



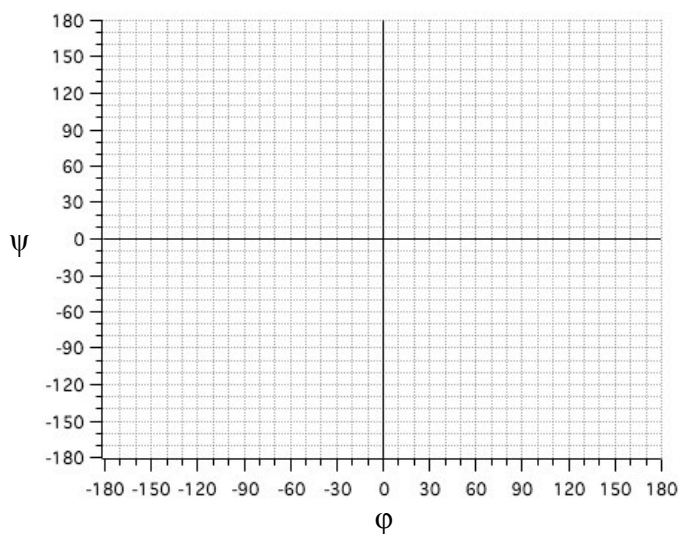
- Using the graph provided above, draw the titration curve for a 200 mM solution of GHK-Cu. Label each of the endpoints with the net charge of the predominant species at that  $pH$ .
- Generally, the solubility of peptides in water will increase along with the *net charge* on a peptide. At what  $pH$  do you expect GHK-Cu to be *least soluble*? \_\_\_\_\_

- h. The GHK-Cu represents one out of how many possible tripeptide sequences that can be made from the standard set of 20 amino acids. (Show your calculation.)  $n =$  \_\_\_\_\_
4. In 2002, bacteriorhodopsin was featured as the Protein Data Bank's *Molecule of the Month*. Bacteriorhodopsin is a compact molecular machine that pumps protons across a membrane and is powered by green sunlight. It is synthesized by halophilic (salt loving) bacteria found in high-temperature brine pools. They use sunlight to pump protons outwards across their cell membranes, making the inside 10,000-fold more alkaline than the outside. These protons are then allowed to flow back into the cell through another protein, ATP synthase, creating much of the ATP that powers the cell..

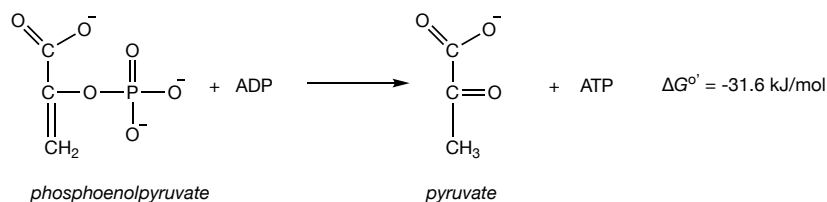


- a. In the 3-D model of the bacteriorhodopsin shown above as a cartoon model. Bound to this protein is the light-absorbing molecule *retinal*. It is shown as a spacefilling model, where the spheres have radii equal to each atom's vander Waals radius. Describe how the vander Waal radius is related to intermolecular interactions.

- b. On the  $\phi/\psi$  plot provided, shade the region where you expect the *majority* of the  $\phi/\psi$  angle pairs to be found for the bacteriorhodopsin protein.
- c. What is the name used to describe this type of plot?
- \_\_\_\_\_



- d. What role does secondary structure play in the folding of the bacteriorhodopsin protein
- e. Retinal is a member of a group of molecules called isoprenoids and is related to the visual pigments found in your eye. Retinal contains two functional groups. On the structure of retinal shown above, circle and label an example of each of these functional groups.
5. In class we look at the structure of the enzyme *pyruvate kinase*, as an example of a protein that has multiple domains. The reaction catalyzed by this enzyme is shown below. It is the last reaction in the glycolytic pathway and transfers a phosphate group from *phosphoenolpyruvate* to ADP to produce *pyruvate* and ATP. (ADP and ATP are abbreviations for the ribonucleotides adenosine diphosphate and adenosine triphosphate, respectively.)



- a. Determine the equilibrium constant for this reaction under standard state conditions at 37°C.  
 $K_{eq} =$  \_\_\_\_\_
- b. Is this reaction favorable (spontaneous) under standard state conditions? (Y/N?) \_\_\_\_\_  
 Explain: \_\_\_\_\_
- c. If the cellular concentrations of reactants and products for this reaction are  
 $[phosphoenolpyruvate] = 23\mu\text{M}$ ,  $[pyruvate] = 51\mu\text{M}$ ,  $[\text{ADP}] = 0.10\text{mM}$ , and  $[\text{ATP}] = 1.0\text{mM}$ , is  
 this reaction favorable under cellular conditions (Y/N)  
 What is your evidence for this claim?: \_\_\_\_\_